A Thesis on

SIMULATION OF 2D RISER REGENERATOR

Submitted By

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CERTIFICATE

This is to certify that the thesis titled ***"Simulation of 2D Riser Regenerator"***, submitted to the National Institute of Technology, Rourkela by **A.Srikrishnan,** Roll No**: 211CH1034** for the award of the degree of **Master of Technology** in Chemical Engineering, is a bonafide record of research work carried out by her under my supervision and guidance. The candidate has fulfilled all the prescribed requirements. The thesis, which is based on candidate's own work, has not been submitted elsewhere for a degree/diploma.

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ABSTRACT

Riser regenerators are regenerating vessels used for removing the coke deposited on the catalyst and provide heat of reaction for the cracking process. Coke formation is unavoidable in the catalytic cracking process, which is probably formed by the dehydrogenation and condensation of polyaromatic and olefins. Fast deactivation by blocking the active pores of the catalyst is a consequence of coke deposition. Riser regenerators are used for regenerating spent FCC catalyst by burning the coke deposited on the catalyst body. These are better compared to the conventional turbulent fluidised beds due to large capacities, higher gas-solid contact efficiency, high heat and mass transfer rates and low solids inventory. These regenerators also offer advantages over conventional scale reactors such as reaction speed, greater combustion of coke, reliability, cost effective, scalability and better safety and control. The present work is aimed to study the behaviour of regeneration reaction of coke inside riser regenerator. The advantages of multiple air inlet riser regenerator have been found out by studying the phenomenon inside the regenerator. The transient simulation has been carried out. The transient solution shows the species concentration and temperature profile inside the riser regenerators. The result reveals that the temperature of the gas increases with axial length and species concentration decreases. It has been found that multiple air inlet regenerator provide a better combustion than the single inlet regenerator.

Keywords: Riser regenerator, FCC catalyst, coke

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NOMENCLATURE

ρ	density of fluid
P	static pressure
Δ	Gradient
E	activation energy
μ	Viscosity
v	velocity
t	time
g	acceleration due to gravity
Y_i	Mass fraction
D	diffusion coefficient
Sc	Schmidt number
M	molecular weight
ν	stoichiometric coefficient
C	concentration
η	rate exponent
T	temperature
Ɛ	volume fraction
R	rate of the reaction
k	rate constant

Subscripts

j	species
t	turbulent
r	reaction
p,q	phase

CHAPTER 1

INTRODUCTION

Chapter 1

INTRODUCTION

Riser regenerators are regenerating vessels used for removing the coke deposited on the catalyst and provide heat of reaction for the cracking process. It is essentially in the form of tall cylindrical vessels wherein the height of the column is much larger compared to the diameter and operated in plug flow. During catalytic cracking the feed is vaporized and the long - chain molecules are cracked into much shorter molecules by contacting the feed with a fluidized powdered catalyst at high temperature and moderate pressure. Coke formation is unavoidable in the catalytic cracking process, which is probably formed by the dehydrogenation and condensation of polyaromatics and olefins. Fast deactivation by blocking the active pores of the catalyst is a consequence of coke deposition. Riser regenerators are used for regenerating spent FCC catalyst by burning the coke deposited on the catalyst body. These are better compared to the conventional turbulent fluidised beds due to large capacities, higher gas-solid contact efficiency, high heat and mass transfer rates and low solids inventory. These regenerators also offer advantages over conventional scale reactors such as reaction speed, greater combustion of coke, reliability, cost effective, scalability and better safety and control.

Riser regenerators can remove greater amount efficiently than fluidised beds. Due to greater combustion of coke a large amount of heat is released during the process, this results in hydrothermal deactivation of catalysts. The temperature inside the regenerator can be modified by providing multiple air inlets or by two stage regeneration. The other modified type of riser regenerator, depending on nature of the feed, solids inventory and product selectivity the type of the regenerator is chosen. Multiple air inlet regenerators provide a

better control and stability than the single inlet type. The riser regenerators are operated usually in fast fluidisation regime (Bai et al, 1997).

1.1 ADVANTAGES OF RISER REGENERATOR

Some of the advantages of riser regenerator are given below (Bai et al):

High coke combustion efficiency: The coke combustion efficiency for a riser regenerator is found to be greater than high efficiency tank or conventional two stage regenerator. The coke combustion efficiency of riser regenerator is > 1000 kg/ton.hr whereas for high efficiency tank is from 200-500kg/ton.hr and that for a conventional two stage regenerator is 100-300 kg/ton.hr.

Efficient mixing: The riser is operated in fast fluidization or pneumatic transport regime the solids are efficiently transported and there is no agglomeration of the solid particles in the riser. The high velocity and effective transport give rise to proper mixing resulting in high heat and mass transfer ratio. It also results in effective combustion of coke from the spent catalyst.

Low solids inventory: The catalysts in the riser geometry are continuously regenerated. The low residence time, high combustion efficiency and absence of any dense bed results in low solids inventory.

1.2 NOVEL DESIGNS OF RISER REGENERATOR

Depending on the plant operation, feed type, cost schemes, efficiency, product selectivity and other environmental constrains there are different novel designs of riser geometry. The common one is the single inlet riser regenerator. With improved flexibility and stability there

is also multiple air inlet riser regenerator. The third type is the two stage riser regenerator, which has an additional heat exchanger in between the two stages. It incorporates the high capacity riser regeneration and staged operation of conventional two stage regeneration. The regenerators types discussed have now been patented in China.

1.2 COMPUTATIONAL FLUID DYNAMICS

Fluid (gas and liquid) flows are governed by partial differential equations (PDE) which represent conservation laws for the mass, momentum and energy. Computational Fluid Dynamics (CFD) is used to replace such PDE systems by a set of algebraic equations which can be solved using digital computers. The basic principle behind CFD modelling method is that the simulated flow region is divided into small cells. Differential equations of mass, momentum and energy balance are discretized and represented in terms of the variables at any predetermined position within the or at the centre of cell. These equations are solved iteratively until the solution reaches the desired accuracy (ANSYS Fluent 13.0). CFD provides a qualitative prediction of fluid flows by means of

- mathematical modelling (partial differential equations)
- numerical methods (discretization and solution techniques)
- software tools (solvers, pre- and post-processing utilities)

1.3.1 ANSYS FLUENT SOFTWARE

FLUENT is one of the widely used CFD software package. ANSYS FLUENT software contains the wide range of physical modelling capabilities which are needed to model flow, turbulence, reactions and heat transfer for industrial applications. Features of ANSYS FLUENT software:

- TURBULENCE: ANSYS FLUENT offers a number of turbulence models to study the effects of turbulence in a wide range of flow regimes.
- MULTIPHASE FLOW: It is possible to model different fluids in a single domain with FLUENT.
- ACOUSTICS: It allows users to perform sound calculations.
- REACTING FLOW: Modelling of surface chemistry, combustion as well as finite rate chemistry can be done in fluent.
- MESH FLEXIBILITY: ANSYS FLUENT software provides mesh flexibility. It has the ability to solve flow problems using unstructured meshes. Mesh types that are supported in FLUENT includes triangular, quadrilateral, tetrahedral, hexahedral, pyramid, prism (wedge) and polyhedral. The techniques which are used to create polyhedral meshes save time due to its automatic nature. A polyhedral mesh contains fewer cells than the corresponding tetrahedral mesh. Hence convergence is faster in case of polyhedral mesh.
- DYNAMIC AND MOVING MESH: The user sets up the initial mesh and instructs the motion, while FLUENT software automatically changes the mesh to follow the motion instructed.
- POST-PROCESSING AND DATA EXPORT: Users can post-process their data in FLUENT software, creating among other things contours, path lines, and vectors to display the data.

1.3 OBJECTIVES OF THE PRESENT STUDY

The objective of the present work is to study the following aspects:

- To explore combustion and hydrodynamic modelling of single air inlet riser regenerator using computational fluid dynamics.
- To study the parameters such as species concentration and temperature for a multiple air inlet riser regenerator using computational fluid dynamics.

1.4 PLAN OF THE THESIS

Chapter 1 represents the complete introduction of the present study including the definition of riser regenerator, its advantages and novel designs and role of computational fluid dynamics.

Chapter 2 deals with the literature review of riser regenerator. This chapter is divided into the sections namely, regeneration and regenerator design, coke burning kinetics and Riser regenerator.

Chapter 3 comprises of modelling equation of single phase and multiple phase flow. The model equation includes the equation of continuity, momentum and energy.

Chapter 4 represents the study of single air inlet riser regenerator using CFD. Here combustion of coke is taken as model reaction. A two-dimensional computational fluid dynamics model of a single air inlet riser regenerator is solved to study the combustion and hydrodynamic characteristics.

Chapter 5 constitutes the study of multiple air inlet riser regenerator using CFD. A comparison is made between the single and multiple inlet riser regenerators.

Chapter 6 deals with the overall conclusion.

CHAPTER 2

LITERATURE REVIEW

Chapter 2

LITERATURE REVIEW

This chapter deals with the literature review of Riser regenerator and it is divided into three sections:

- Regeneration and Regenerator design
- Coke combustion kinetics
- Riser Regenerator

2.1 REGENERATION AND REGENERATOR DESIGN

The main purpose of the regenerator is to remove the coke from the spent catalyst coming from the reactor. The catalyst activity of the fluidized particles is thereby re-established prior to being returned to the reactor riser. This also results in the recovery of surface area and porosity. To be suitable for regeneration, the content of contaminant metals in spent catalyst should not exceed 5 wt. %. Otherwise, at least 80% recovery of the original activity to make regeneration attractive may not be achieved. Early designs were of the bubbling-bed type with superficial gas velocities in the regenerator bed of less than 1 ft. /sec. The temperature in the regenerator bed was typically in the 1200-1250°F range. Commercial regenerations are now typically run at higher superficial gas velocities in the turbulent-bed or fast-fluidized-bed regimes along with operating temperatures up to 1400°F. One of the key factors in regenerator design is a thorough understanding of the regenerator heat balance. The heat released from the combustion of coke is the largest single component in the regenerator heat balance and in the overall FCCU heat balance as well. Under properly controlled regenerating conditions, almost complete removal of carbon deposited on catalyst can be achieved. The oxidative regeneration using air is the most commercially used method for regeneration.

There have been various types of regenerator depending on the company and based on various fluidization regimes. Early in 1950s' UOP (Universal Oil Products) along with Mobil developed the high efficiency riser-regenerator. It is interesting to note that the Mobil-UOP high-efficiency FCC unit contained all major fluidization regimes. Despite its relatively low significance commercially, the bubbling regime has attracted considerable attention in academia and still finds applications in design of various pilot plants. In 1951, Kellogg began offering its Orthoflow design (Orthoflow "A") with the reaction and regeneration zones superposed within a single vessel. A joint Mobil-UOP effort to commercially develop a new FCC process design was started in 1970. The unit was an early version of the present high-efficiency FCC unit. The units later installed by Mobil were riser reactors with "shave-off" cyclones, dual feed injection, and high-efficiency regenerators capable of converting the entire CO to CO_2. Current designs use dense-phase down flow of solids, controlling heat removal by adjustments in aeration to the exchanger, which directly affects catalyst-side heat transfer. Catalyst returns to the regenerator through a lift line, and circulation depends on relative densities in the cooler loop, without use of a slide valve. Many basic principles will probably be retained, but the evolutionary process which has been responsible for past progress will continue. Yet, there is room for real breakthroughs. (Amos and Hartley et al, 1990)

Babich et al., (2005) studied the nature of species and their role in NOx formation during FCC regeneration. The pyridinic N type compounds present in the outer layers of catalyst reduced even in presence of high C or CO. The 'Q-N type' compounds adsorbed in the inner parts of the catalyst mainly at the acid sites is combusted last. It was found that absence of reducing agents (CO & CO_2) resulted in the conversion of these compounds to NOx during FCC regeneration.

Iliopoulou et al., (2004) experimented on the effect of Rh-based additives on NO and CO formed during regeneration of spent FCC catalyst. The Rh based catalyst was supported on alumina with Cerium. The effect was compared with the conventional Pt based CO promoter. It was found that a combined performance of CO oxidation and NO reduction was achieved with minimized Rh loading in the additive (0.1 wt. %) and the concentration of additive used during regeneration (1 wt. %). The NO reduction by CO over Rh/alumina additives proceeded via the dissociative adsorption of NO, the formation of N-CO species on Rh and their migration to the alumina support to yield N_2 and CO_2.

Kanervo et al., (2001) worked on regeneration kinetics of a cracking catalyst by temperature programmed oxidation (TPO) in a micro reactor system. The CO and CO_2 responses were detected as a function of time on heating at a constant rate. Different oxygen concentrations (0.5–2.0%) and heating rates (5 and 10 K/min) were applied. Three kinetic models were tested and the parameters were estimated by non-linear regression. The smallest sum of squared residuals was obtained showed that the formation of CO and CO_2 proceeded via a common oxygen-containing intermediate.

Bollas et al., (2006) studied the integrated FCC riser—regenerator dynamics in a fluid catalytic cracking pilot plant. Simulations were performed according to the two-phase theory of fluidization; a dilute phase model with post combustion reactions was performed. The process variables such as the reaction conversion, the coke yield, the carbon on regenerated catalyst and the catalyst circulation rate were used for the validation of the steady-state performance of the simulator. The comparison between the dynamic responses of the model and those of the pilot plant to step changes in the feed rate and preheat temperature revealed the ability of the simulator to accurately depict the complex pilot process dynamics in both open and closed-loop operation.

Corma et al., (2011) studied the Coke steam reforming in FCC regenerator with high coking tendency. The process used heavy feeds and the heat balance in the unit is maintained by removing the high coke-on-catalyst by coke combustion and reforming. This enabled using feeds with more than 10% Conradson Carbon and controlled the heat balance in the unit without using partial combustion or catalyst coolers. The reaction rate at higher temperatures was found to obey first order, steam reforming coke removal kinetics at lower (750 °C) temperatures found to be more complex due to the heterogeneous nature of coke.

Doolin et al., (1991) experimented on the role of metal contaminants in the production of carbon dioxide during the regeneration of cracking catalysts. The factors which affected the ratio of combustion products in the flue gas from a catalytic cracking unit were investigated. Units which processed resids found to suffer feed throughput due to high CO_2/CO ratios. The effect of contaminant metals (nickel, vanadium and iron) on the combustion of carbon in the regenerator was also studied. The metal activity for the production of carbon dioxide increases from iron < vanadium > nickel. Results show that nickel catalyses carbon directly to carbon dioxide. Therefore, the amount of active nickel should be minimized to prevent high CO_2/CO ratios in the regenerator. The active catalytic species should be passivated by antimony when nickel and antimony are allowed to interact under reducing conditions.

Chang et al., (2013) studied the CFD modelling of hydrodynamics, heat transfer, and coke combustion in an industrial turbulent fluidized-bed FCC regenerator based on the Eulerian-Eulerian model. A CFD model including heat transfer and coke combustion reactions were established. The detailed hydrodynamics, temperature, and species concentration distribution inside the regenerator were found under various operating conditions. The simulation result showed that the flow behaviour in the regenerator was more turbulent disorder, causing the axial and radial non uniformity of catalyst content, temperature, and species concentration. Increasing the operating pressure and superficial gas velocity accelerated the coke

combustion, better efficiency. However, the increase in initial coke content and spent catalyst circulation rate deteriorated the regeneration performances. The simulated regenerator could not burn more coke due to limited coke-burning capacity.

Ozawa et al., (1969) simulated the adiabatic regeneration process in fixed beds at lower temperatures. At lower temperatures, the burning rate was controlled by the intrinsic chemical kinetics, due to higher activation energy than the mass transfer-controlled regime. The higher temperature dependence of the rate constant caused a significant difference in the temperature and concentration profiles compared to the conventional regeneration process. An implicit semi- analytical solution for the quasi-steady-state burning regime was shown to be approached by the unsteady-state solution asymptotically for larger times. The semi-analytical solution greatly reduces the numerical solution time required for simulating the entire burning period.

Zhao et al., (1997) studied the emission on NOx from FCC regenerator. The study involved the transformation of nitrogen species during cracking and regeneration process. Data was obtained from the pilot plant and was shown that thermal NOx does not contribute to NOx emission. The use of direct NOx reduction additives and a new generation of CO combustion promoters significantly reduced NOx. The results were compared between industrial and laboratory and found to be satisfactory with the NOx chemistry.

Sheikh et al., (2008) studied the mathematical models and simulations of an integrated downer-regenerator FCC unit. Simulations results for the downer type unit were partially validated against data collected in a 0.1-0.3 b/day pilot plant that was operated in the high-severity mode. The model predicted temperature profiles along the regenerator. The difference between model predictions and actual regenerator temperatures was found to be 6%.

Rebel and Huang et al (1990) studied the detail kinetic description of the kinetics in both the reactor and the regenerator using the full range of published data both on FCC performance and kinetic rates. They described the effect of catalytic combustion promoters in combustion kinetics.

Wen et al., (2002) worked on the simultaneous catalytic removal of NOx, SOx, and CO under simulated FCC regenerator conditions over mixed oxide catalysts CuMgAlO (Cu-cat), CeMgAlO (Ce-cat),and CuCeMgAlO (CuCe-cat), which were prepared by co-precipitation and characterized by XRD,XPS, and N_2 adsorption-desorption. It was found that at low temperatures (<340 °C), the presence of O_2 or H_2O enhanced the activity of CuCe-cat for NO and CO conversion but significantly suppressed the activity of Cu-cat and Ce-cat. At high temperature (720 °C), the presence of O_2 or H_2O had no adverse effect on the NO and CO conversions over these catalysts. However, the presence of SO_2 in the feed deactivated Cu-cat and Ce-cat drastically while no deactivation of CuCe-cat was observed. The enhanced performance of CuCe-cat is due to a synergistic effect between copper and cerium ions, which results in the formation of large amounts of Cu+ ions and oxygen vacancies.

Fernandes and Pinheiro et al (2007) worked on enhanced model for the reactor-regenerator system of a UOP fluid catalytic cracking (FCC) unit with a high-efficiency regenerator. A different cracking deactivation model is considered, and the freeboard region in the regenerator vessel was also explicitly addressed. The resulting model was fitted to industrial data, using new correlations to estimate the cracking kinetic constants and other important parameters in the FCC heat balance. The parameter estimation allowed a good agreement between the simulated results and the available industrial data.

2.2 COKE-BURNING KINETICS

The coke deposited on the catalyst consists primarily of carbon and hydrogen along with relatively small amounts of sulfur, nitrogen, and metals. With the use of high conversion, zeolite catalyst and modern stripper designs, the amount of hydrogen in coke has typically decreased over the years to levels of 6-7 wt.% .Catalyst regeneration, as a carbon removal process, is widely accepted as being described by a first order kinetics expression with respect to carbon concentration and oxygen partial pressure.

$$\frac{dC}{dt} = KCP_{o2} \qquad 2.1$$

K = Rate constant, atm $hr.^{-1}$

C = Carbon on catalyst, wt. %

Po_2 = Oxygen partial pressure, atm

The reaction rate constant will depend on temperature and can be expressed in an Arrhenius type-equation:

$$-\frac{dC}{dt} = K_o e^{-\frac{\Delta E}{RT}} CP_{o2} \qquad 2.2$$

ΔE = Activation energy

R = Gas constant

T = Temperature

Diffusion to and from the catalyst surface and within the catalyst pores did not limit the carbon- burning rate. The oxidation of hydrogen, however, proceeds more rapidly than that of carbon. The rate of carbon burning depends on the carbon level on the catalyst and the

temperature of the catalyst. The catalyst temperature, in turn, depends on the amount of carbon and hydrogen burned, because the heat of combustion of these components raises the catalyst temperature.

Barth and Jentys et al (1992) studied the surface chemistry of coke precursors on the spent fluid catalytic cracking catalysts during the oxidative regeneration process by temperature-programmed desorption, temperature-programmed oxidation experiments and IR spectroscopy. NH_3 and HCN were formed via cracking and hydrolysis reaction of coke above 350 °C. The amount of NH_3 released depended on the concentration of water in the samples. The presence of 5% water significantly lowered the amount of coke N (40% vs. 74%) was converted to NOx during the regeneration process. Temperature-programmed oxidation experiments indicated that polyaromatic nitrogen compounds were cracked to CO and HCN, which oxidized in part to NO. The addition of Pt-based CO combustion promoters enhanced the oxidation of reduced nitrogen intermediates and leads to an increased NO emissions.

Dimitriadis et al., (1992) worked on the combustion kinetics of carbon in carbonaceous deposits, or ‘ coke’ , on fluid catalytic cracking (FCC) zeolite catalysts under differential reactor conditions, in an air stream, at atmospheric pressure, and in a temperature range of 710°C. Catalysts with and without Pt were first coked and then subsequently regenerated. Experimental findings revealed the lack of any catalytic effect of Pt on carbon burning rates. The equilibrium catalyst from a commercial FCC unit catalyst exhibited higher burning rates than catalysts containing coke deposited in a laboratory reactor. The higher burning rate was due to the high metal content of heavy metals like V and Ni.

Stevenson et al., (2005) collected data on the emissions of NO, HCN, and N_2 during the regeneration of spent fluid catalytic cracking catalyst in two different laboratory-scale units.

Two models were developed, first model described the combustion of coke due to the volatilization of nitrogen as HCN, which oxidizes to NO or hydrolysed to NH_3. The presence of coke reduces NO to N_2 .The reaction is accelerated by the presence of CO.

Roncolatto et al., (2007) studied the evolution of carbon (C) and nitrogen (N) in a spent (coked) fluid catalytic cracking (FCC) catalyst during regeneration. A commercial spent FCC catalyst from a refinery was submitted to calcination procedures with air, and samples were collected at different temperatures and times. These were analysed by X-ray photoelectron spectroscopy (XPS) before and after milling to follow the variation of C and N contents in the surface. It was observed that both C and N are preferably located on the external FCC catalyst surface. For a total C amount of 1.3 wt. %, the C content on the surface is about 18.3 wt. %. The surface N present in coke was found to be 1.4 wt. %, which is 176 ppmw.

Henrique and Carsten et al (2005) worked on the characterization of industrial coked resid fluid catalytic cracking (RFCC) catalysts. The work provided insight into the coke deposition on commercial resid fluid catalytic cracking catalysts sampled after the stripper of a commercial RFCC unit and its potential process chemistry. Physicochemical techniques were used to characterize the used catalysts and the deposited coke. About 95% of the coke was insoluble in CH_2Cl_2. The coke was located in the mesopores of the catalyst matrix. The results also suggested the existence of domains of polyaromatic and heterogeneously distributed coke, in which saturated hydrocarbons were trapped. IR spectroscopy showed the largest fraction of strong Bronsted acid sites was free after the catalyst had passed the stripper. The results indicated that for RFCC not the local deactivation of the acid sites but rather blocking of domains of the catalyst was the most important mode of deactivation after passing through the riser reactor.

Yunhau et al., (2006) studied the burning properties of carbon particles in clusters numerically using a mathematical model. Chemical reactions consisted of heterogeneous reactions including char combustion and in gases homogeneous reactions. The numerical model predicted gas the flux through a cluster, distributions of gas temperature and concentrations of gas species in clusters. Burnout of char particles in cluster was found to be lesser than that of isolated char particles in the stream. Formation of NO and N_2O were restrained from particle clustering.

Andres et al., (2003) studied the effects of sweeping treatment on the activity recovery, coke content, H/C ratio and kinetics of coke combustion on HZMSM-5 zeolite. The reaction studied was the transformation of acetone to hydrocarbons at 400° C .The gases used in the sweeping are He, H_2 and steam. Sweeping with H_2 caused catalyst rejuvenation, that with He promoted coke aging and a reduction in H/C ratio. The coke elimination with steam caused de-alumination.

Pierre et al., (2001) studied on coking and deactivation of HFAU, HBEA and HMFI zeolites with Si/Al ratio of 15 with methyl cyclohexane transformation at 450° C at different contact times. Coking was found to be faster on HBEA than on HMFI and on HFAU, whereas the deactivating effect of coke was more pronounced on the latter zeolite. Coke was found to be a secondary product resulted from the transformation of the apparent primary aromatic and olefinic products. The differences in the mode of deactivation were related to large differences in the crystallite sizes.

Corma et al., (2007) worked on several catalysts by increasing initial coke content to assess the activity and selectivity of coked catalysts. Tests were conducted at constant operating conditions and for different cat/oil ratio. It was found that coke on regenerated catalyst has

little influence on the main product selectivity. The change had been due to the hydrogen transfer to cracking rate as it lowered the site density.

2.3 RISER REGENERATOR

Riser Regeneration technology is an emerging field with applications in most industrial processes due to controlled reaction environment, combustion efficiency and excellent mixing. This technology offers improvements in existing processes and enables the process to become cost effective. Still lot of development and research is to done in this area.

Bai et al., (1997) proposed two novel designs of FCC riser regeneration. The first design allowed the regenerating air to be separately supplied at several different levels in the riser, the second design is a two-stage riser FCC regenerator, which connected two riser regenerators in series. This novel design combined the advantages of both the riser regeneration and the conventional two-stage turbulent bed regenerator. It also provided significant advantages over the single riser regenerator.

Bai et al., (1998) designed a comprehensive one-dimensional model for the simulation of a riser regenerator. The model incorporated the hydrodynamic characteristics of fluidized bed risers and the detailed reaction kinetics of FCC catalyst regeneration and can be used to predict the axial profiles of temperature, oxygen concentration and coke content of the catalyst in the riser. The validity of model was confirmed by the experimental data from a pilot demonstration unit. The simulation results have provided the necessary information for the optimal design and operation of a FCC riser regenerator unit, presently in operation in China.

Xiancheng et al., (2007) worked on a post-riser regeneration technology (PRRT) for fluid catalytic cracking (FCC) units to deal with increasingly heavier feedstock and thereby increasing the amount of coke deposited on the catalyst particles during reaction. The technology made full use of the advantages of riser regenerator, such as high coke burning efficiency and low residual carbon, and at the same time overcome its disadvantages, such as difficulty in starting combustion. The average particles concentration on the cross section of the system was studied on a large scale cold model experimental set-up. The necessary software was developed by combining the hydrodynamics research results in our work with the coke-burning kinetics model and the heat and mass transfer model developed by previous researchers. The simulation results showed that the PRRT could increase regeneration capability by 16.28%–26.24% over the conventional turbulent fluidized bed regenerator under the similar operation conditions, and that the residual carbon could be kept below 0.1 wt. %.

CHAPTER 3

COMPUTATIONAL FLUID DYNAMICS MODEL EQUATIONS

Chapter 3

COMPUTATIONAL FLUID DYNAMICS MODEL EQUATIONS

In this chapter the computational fluid dynamics modelling equations are described for single and multiphase system. Besides, reaction modelling equations are also mentioned. The theory for the system is taken from the ANSYS Fluent 13.0.

3.1 FLOW MODELLING

THE MASS CONSERVATION EQUATION

The equation for conservation of mass or continuity equation can be written as follows:

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho.\mathrm{V}) = 0 \tag{3.1}$$

Above equation is the general form of the mass conservation equation .

MOMENTUM CONSERVATION EQUATIONS

The conservation of momentum equation is given by

$$\frac{\partial(\rho V)}{\partial t} + \nabla.(\rho.V.V) = -\nabla.P + \nabla.(\tau) + \rho g + F \tag{3.2}$$

where, p is the static pressure, τ is the stress tensor, and g and F are the gravitational body force and external body forces (e.g., that arise from interaction with the dispersed phase), respectively. F also contains other model-dependent source terms such as porous-media and user-defined sources.

$$\tau = \mu\,[\,(\nabla V + \nabla V^{T}) - \frac{2}{3}\nabla.v.I\,] \tag{3.3}$$

Where μ is the molecular viscosity, I is the unit tensor, and the second term on the right hand side is the effect of volume dilation.

SPECIES TRANSPORT EQUATIONS

$$\frac{d(\rho Y_i)}{dt} + \nabla.(\rho.\overline{V}Y_i) = -\nabla.\overline{J_\iota} + R_i + S_i \quad (3.4)$$

Ri is the net rate of production of species i by chemical reaction and Si is the rate of creation by addition from the dispersed phase plus any user-defined sources. An equation of this form will be solved for N-1 species where N is the total number of fluid phase chemical species present in the system. Since the mass fraction of the species must sum to unity, the Nth mass fraction is determined as one minus the sum of the N-1 solved mass fractions.

Mass Diffusion in Laminar Flows

Ji is the diffusion flux of species i, which arises due to concentration gradients.

$$\overline{J_i} = -\rho D_{i,m} \nabla Y_i \quad (3.5)$$

Mass Diffusion in Turbulent Flows

$$\overline{J_\iota} = -\left(\rho D_{i,m} + \frac{\mu_t}{Sc_t}\right) \nabla Y_i \quad (3.6)$$

3.2 REACTION MODELLING

3.2.1 LAMINAR FINITE-RATE MODEL

The laminar finite-rate model computes the chemical source terms using Arrhenius expressions, and ignores the effects of turbulent fluctuations. The net source of chemical species i due to reaction is computed as the sum of the Arrhenius reaction sources over the NR reactions that the species participate in:

$$R_i = M_{w,i} \sum_{r=1}^{N_r} \overline{R_{\iota,r}} \quad (3.7)$$

where Mw,i is the molecular weight of species i and Ri,r is the Arrhenius molar rate of creation/destruction of species i in reaction r.

General form of rth reaction

$$\sum_{i=1}^{N} V_{i,r} M_i \leftrightarrow \sum_{i=1}^{N} V'_{i,r} M_i \tag{3.8}$$

For a non-reversible reaction, the molar rate of creation/destruction of species i in rth reaction is given by

$$\overline{R_{\imath,r}} = \tau(V'_{i,r} - V_{i,r})(K_{f,r} \prod_{j=1}^{N} [C_{j,r}]^{(n_{j,r}+n'_{j,r})} \tag{3.9}$$

For a reversible reaction, the molar rate of creation/destruction of species i in reaction r is given by

$$\overline{R_{\imath,r}} = \tau(V'_{i,r} - V_{i,r})(K_{f,r} \prod_{j=1}^{N} [C_{j,r}]^{n_{j,r}} - K_{b,r} \prod_{j=1}^{N} [C_{j,r}]^{n'_{j,r}} \tag{3.10}$$

represents the net effect of third bodies on the reaction rate. This term is given by

$$\tau = \sum_{j}^{N} \gamma_{r,j} C_j \tag{3.11}$$

The forward rate constant for reaction r, is computed using the Arrhenius expression

$$k_{f,r} = A_r T^{\beta r} e^{-\frac{E_r}{RT}} \tag{3.12}$$

If the reaction is reversible, the backward rate constant for reaction r, is computed from the forward rate constant using the following relation:

$$k_{b,r} = \frac{k_{f,r}}{k_r} \tag{3.13}$$

where Kr is the equilibrium constant for the rth reaction.

3.2.2 EDDY DISSIPATION MODEL

Most fuels are fast burning, and the overall rate of reaction is controlled by turbulent mixing. In non-premixed flames, turbulence slowly mixes fuel and oxidizer into the reaction zones where they burn quickly. In premixed flames, the turbulence slowly mixes cold reactants and hot products into the reaction zones, where reaction occurs rapidly. In such cases, the combustion is said to be mixing-limited, and the complex and often unknown, chemical kinetic rates can be safely neglected. The net rate of production of species i due to reaction r, Ri,r is given by the smaller (i.e., limiting value) of the two expressions below:

$$R_{i,r} = \vartheta_{i,r} M_{w,i} A \rho \frac{\epsilon}{k} \min_R \left(\frac{Y_R}{\vartheta_{R,r} M_{w,R}}\right) \quad (3.14)$$

$$R_{i,r} = \vartheta_{i,r} M_{w,i} AB \rho \frac{\epsilon}{k} \min_R \left(\frac{\sum_p Y_p}{\sum_j^N V_{j,r\prime} M_{w,j}}\right) \quad (3.15)$$

where, A and B are empirical constants having values equal to 4.0 and 0.5 respectively. Y_P refers to the mass fraction of product species and Y_R refers to the mass fraction of any particular reactant.

3.3 MODELLING MULTIPHASE FLOW

EULERIAN MODEL

The Eulerian multiphase model in FLUENT allows for the modelling of multiple separate, yet interacting phases. The phases can be liquids, gases, or solids in nearly any combination.

CONSERVATION OF MASS

The continuity equation for phase g is

$$\frac{d(\epsilon \rho_g V_g)}{dx} = 0 \quad (3.14)$$

The continuity equation for phase p is

$$\frac{d[(1-\epsilon)\rho_p V_p]}{dx} = 0 \tag{3.15}$$

CONSERVATION OF MOMENTUM

The momentum balance for phase g is

$$\frac{d(\epsilon\rho_g V_g^2)}{dx} = -\frac{dp}{dx} - F_D - \varepsilon\rho_g g - F_g \tag{3.16}$$

Where $F_D = \frac{3}{4} . \frac{1-\epsilon}{d_p} . C_D . \rho_g . (V_g - V_p)^2$ (3.17)

Taking into account the drag reduction due to solids aggregation, the actual drag coefficient can be obtained by

$$\frac{C_D}{C_{Ds}} = 1.68\ \epsilon^{-0.25}\ \frac{Re_t}{Re_r}^{-1.21}\ \frac{d_p}{D}^{0.11} \tag{3.18}$$

CDS stands for the standard drag coefficient of a single particle in a uniform flow. The frictional shear forces of gas and solids against the wall, Fg and Fp, can be expressed by

$$F_g = \frac{2f_g\rho_g\varepsilon V_g^2}{D} \tag{3.19}$$

$$F_p = \frac{2f_p\rho_p(1-\varepsilon)V_g^2}{D} \tag{3.20}$$

For the problem considered$\rho_g = 1.20\ kg/m^3$,$\rho_p = 1600\ kg/m^3$ and D=80μm.

CHAPTER 4

COMBUSTION AND HYDRODYNAMIC MODELLING OF SINGLE AIR INLET RISER REGENERATOR

Chapter 4

COMBUSTION AND HYDRODYNAMIC MODELLING OF SINGLE AIR INLET RISER REGENERATOR

This chapter deals with the regeneration and hydrodynamics of single air inlet riser regenerator. The riser consists of rectangular geometry with single inlet at the bottom and outlet at the top. A two dimensional computational fluid dynamic model of the riser regenerator is considered.

4.1 PROBLEM STATEMENT

Combustion of coke and hydrodynamics of spent FCC particles is considered. Premixed, non-preheated air and hot coke is fed to the inlet of the riser regenerator. Coke combustion carried out in two different steps, carbon combustion and hydrogen combustion with the assumption that reaction goes to completion without intermediate formation of CO .The rate of reaction of carbon depends on catalyst properties and not on the nature of the feed (Bai et al 1998):

$CH_{12\alpha} + (1 + 3\alpha)O_2 \rightarrow CO_2 + 6\alpha H_2O$ (α= hydrogen to carbon mass ratio in coke)

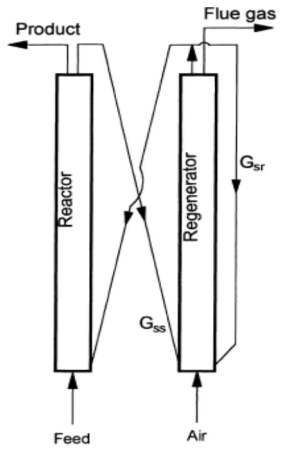

Figure 4.1: Single air inlet Riser regenerator (Bai et al 1998)

Table 4.1: Operating conditions and parameters used in simulation

Parameter	Unit	Value
Length	m	4.0
Width	m	0.3
Coke inlet gap	m	0.1
Inlet air temperature	K	313
Inlet coke temperature	K	723
Inlet mass fraction of carbon		0.4
Inlet mass fraction of hydrogen		0.6
Mass flow rate of catalyst	Kg/s	1
Pre-exponential factor for carbon	sec^{-1}	$1.65*10^{8}$
Pre-exponential factor for H_2	sec^{-1}	$2.44*10^{8}$
Activation energy for carbon	kJ/mole	$1.612*10^{5}$
Activation energy for H_2	kJ/mole	$1.577*10^{5}$
Reaction order		1

4.2 FLUENT SIMULATION

4.2.1 GEOMETRY AND MESH

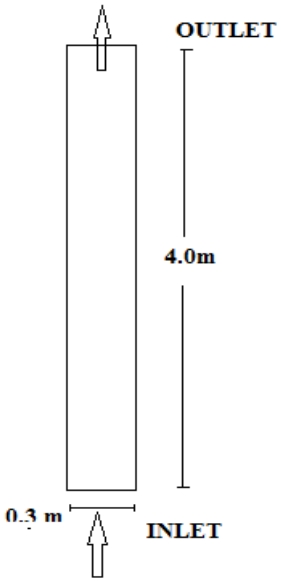

Figure 4.2: Schematic of Computational domain

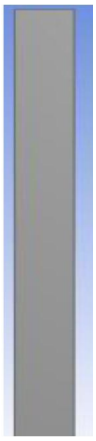

Figure 4.3: Geometry in Ansys workbench 13.0

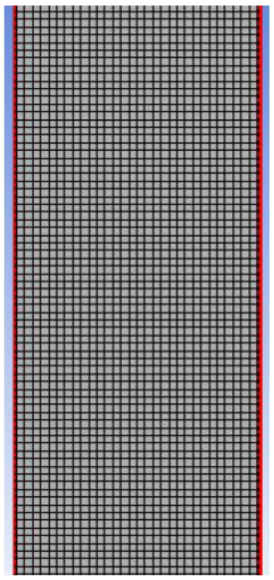

Figure 4.4: Meshing of geometry

A 2D geometry is created by using ANSYS 13 software. The geometry is created in ANSYS workbench. The geometry is meshed into smaller cells. Structured meshing method is used for meshing the geometry. It is meshed into 12431 nodes and 12000 elements.

4.2.2 BOUNDARY AND INITIAL CONDITIONS

In order to obtain a well-posed system of equation, reasonable boundary conditions for the computational domain have to be implemented. At inlet velocity of the gas and coke is specified. Mass flow rate of catalyst and mass fraction of the species are specified. At outlet pressure boundary condition is specified. No slip boundary condition is specified at the wall.

4.2.3 SOLUTION TECHNIQUES

In fluent, solver is set as segregated which solves the equation individually. Transient state simulation has been formulated. Here pressure based solver is used. The species transport model is considered. Laminar finite rate model is used to predict the reaction rate.

The discretization scheme for momentum, turbulent dissipation rate, turbulent kinetic energy and all has been taken as first order upwind.

4.3 RESULTS AND DISCUSSIONS

In this section transient state results are discussed. The concentrations of the species inside the regenerator along axial direction at specified positions are plotted. Further the effect of superficial velocity and solids flow rate on temperature profile along axial directions at specified positions is also plotted. The volume fraction of the solids along axial direction is along discussed.

4.3.1 CONCENTRATION OF CARBON, HYDROGEN AND OXYGEN IN AXIAL DIRECTION FOR SINGLE AIR INLET RISER REGENERATOR

Figure 4.3 shows that with the progress of the reaction the concentration of carbon and hydrogen decreases and the temperature of the system increases. This is resulted due to the high concentration of solids at the entrance and presence of oxygen rich air at the inlet result in high reaction rates. Therefore, there are large axial variations in the reactant concentrations and temperature. Up the riser, Oxygen is largely consumed. As well, solids concentration becomes low and varies little along the axial position. This results in low reaction rates and relatively small changes in the reactant concentrations and temperature along the riser suggesting that the regeneration becomes more difficult up the riser.

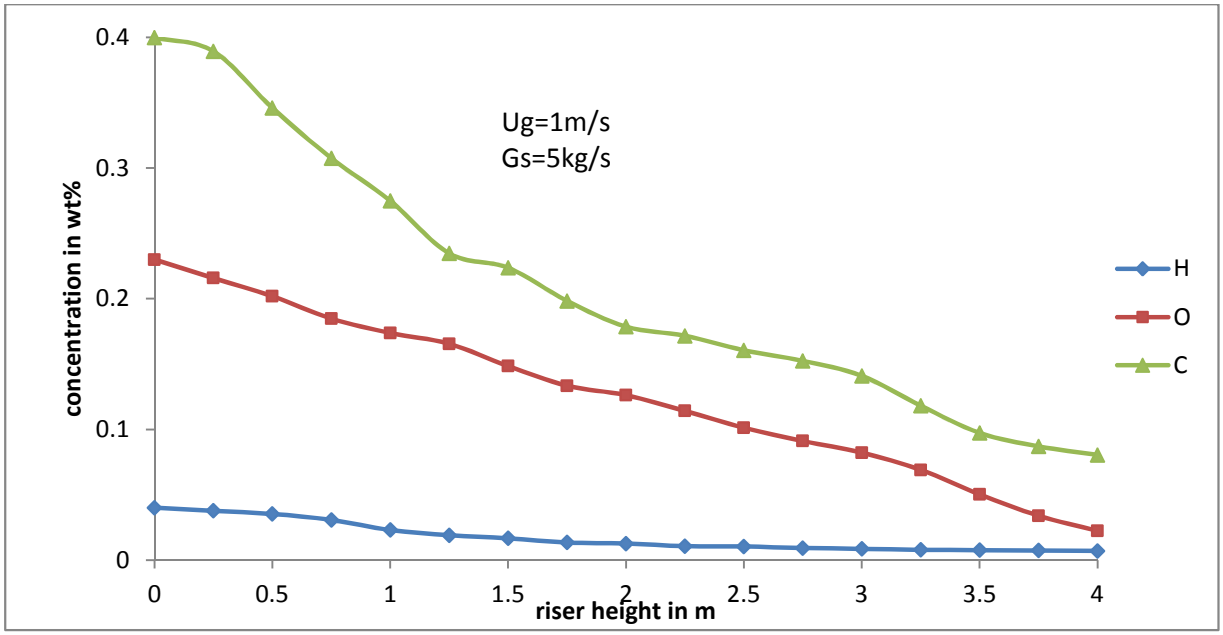

Figure 4.5: Variation of concentration of carbon, hydrogen and oxygen along axial direction.

4.3.2 EFFECT OF SUPERFICIAL VELOCITY AND SOLIDS FLOW RATE ON TEMPERATURE

Superficial velocity and solids flow rate play a major role in the regeneration of catalysts. Increase in superficial velocity increases the amount of oxygen concentration hence; there is an increase in temperature. Higher the velocity the greater the amount of oxygen in the system and more combustion of coke from the spent catalyst. However, increase in superficial velocity continuously reduces the reaction rates due to large amount of heat the gases remove. The removal of heat leads to quenching which ultimately stops the reaction. Increase in solids flow rate increases the temperature, as more and more coke is added to the system. Addition of more spent catalyst result in greater reaction rates. But we have to make sure that the velocity is not too low, which results in accumulation of greater coke in the exit.

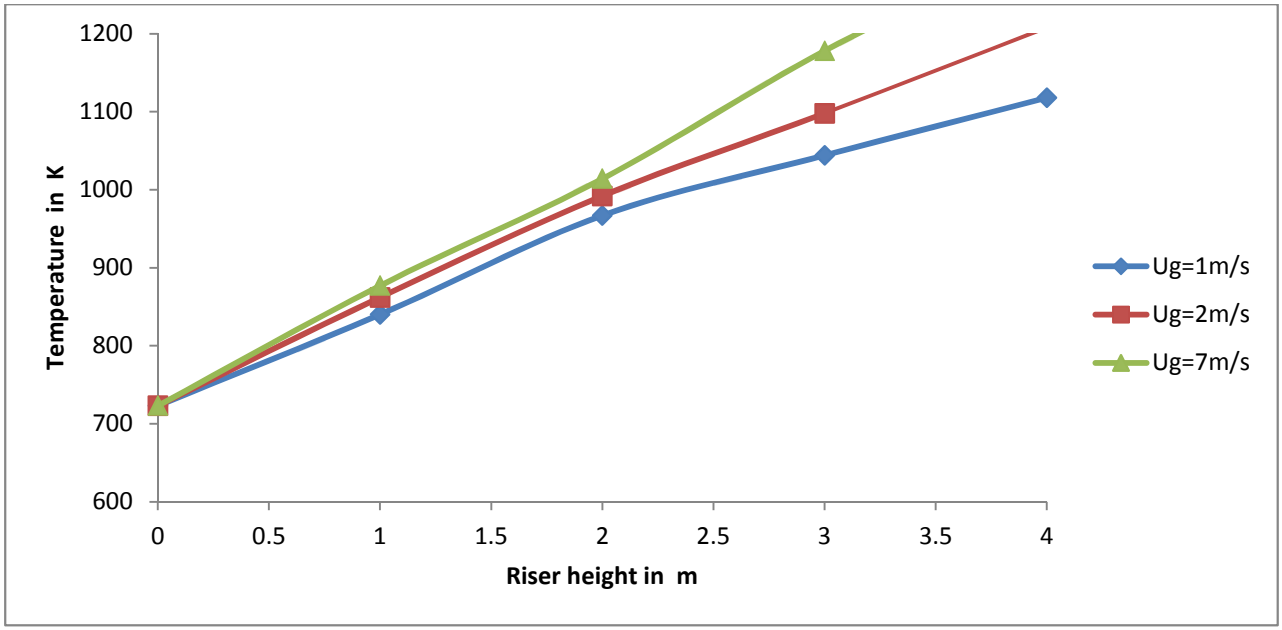

Figure 4.6: Temperature profile in the riser for different superficial velocity along axial direction

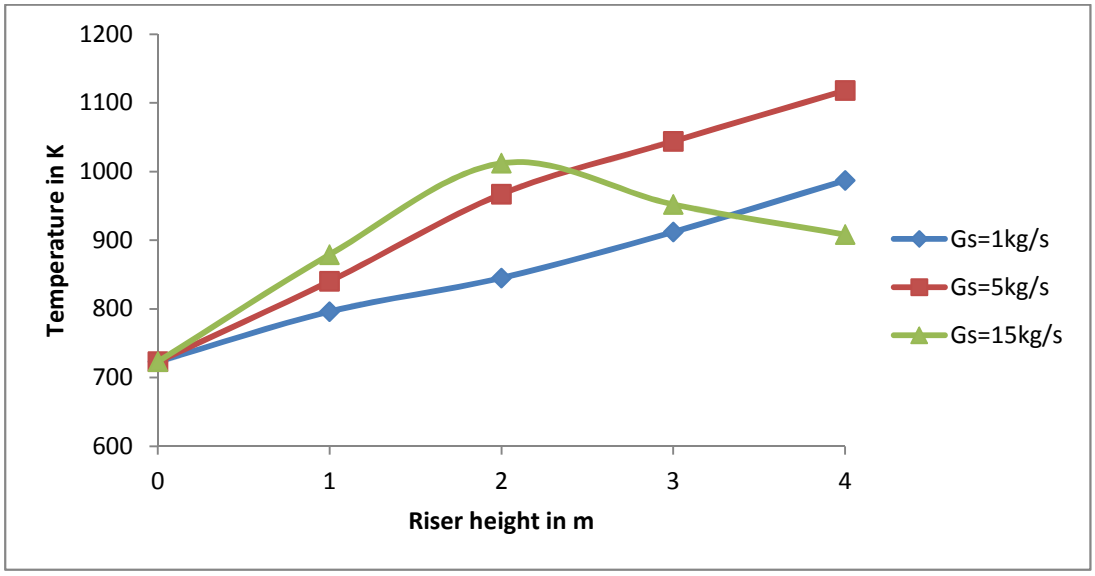

Figure 4.7: Temperature profile for variation for solid flow rate along axial direction

4.3.3 HYDRODYNAMIC STUDIES OF RISER REGENERATOR

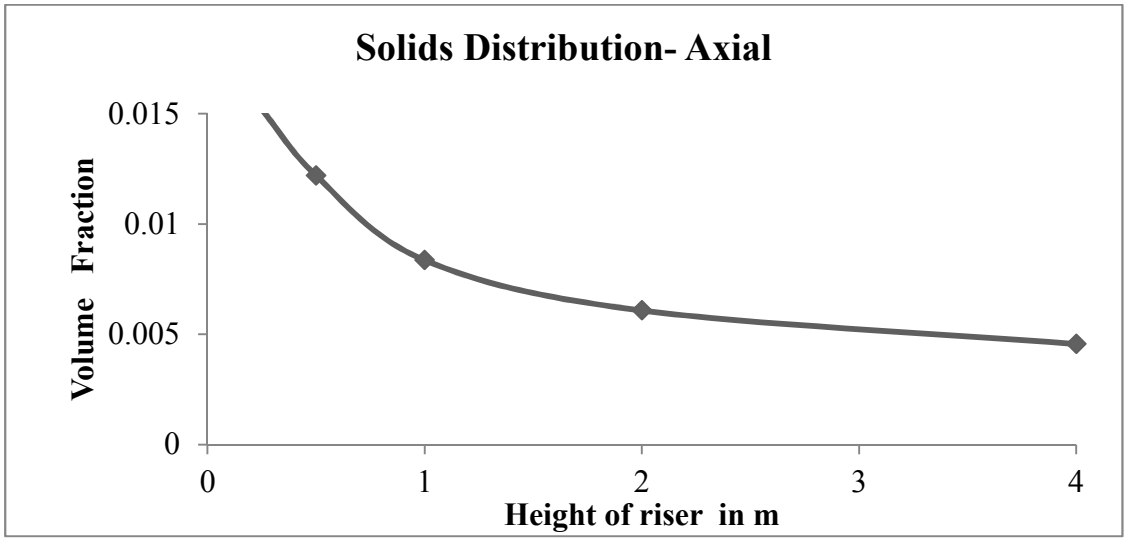

Figure 4.8: Volume fraction of solids in axial direction

The hydrodynamics of the system helps in the understanding the solid – gas interaction in the riser .The figure above shows the volume fraction of the solids along axial direction in the riser geometry. The volume fraction of solids reduces as we move the length of the riser. Initially at the inlet the concentration of solids is high and there is large interaction between the solid and fluid phases. As the riser is normally operation in fast fluidization - pneumatic transport regime, the concentration of the solids decreases as there random transportation of solids. The velocity is found to high especially near the walls of the riser, mainly due to gas bypassing through the centre, which is also a reason for low void fraction.

4.4 CONCLUSION

A numerical study of riser regenerator is discussed. Regeneration of spent catalyst is taken as the model reaction. Key conclusion of this chapter can be summarized as follows:

- The concentration of species decreases along the riser and the temperature inside the riser goes on increasing.
- Increase in superficial velocity increases the reaction rate as long as the temperature does not go below quenching temperature.
- Increase in solids flow rate initially increases but decrease at higher solids concentration due to limiting oxygen concentration.
- The axial concentration of solids is higher at the bottom than at the top.

CHAPTER 5

REGENERATION IN MULTIPLE AIR INLET RISER REGENERATOR

Chapter 5

REGENERATION IN MULTIPLE AIR INLET RISER REGENERATOR

The results have shown that the riser regenerator offers considerable advantages over the conventional turbulent fluidized bed regenerator with high combustion efficiency and intensity. However, the single riser regenerator have some shortcomings, like a long riser is required, which leads to notable heat loss and increased capital investment. In addition, temperature control becomes difficult. With the large amount of heat generation, a lower entrance temperature is preferred, but too low an entrance temperature will quench the operation. On the other hand, a relatively high entrance temperature will lead to a high temperature at the top of the riser, which will possibly result in the hydrothermal deactivation of catalyst due to steaming from hydrogen combustion. In addition, the single riser regenerator lacks the necessary flexibility and stability in its operation industrially. The operating air velocity is very restricted since a low air flow rate cannot supply enough oxygen for the regeneration, but a high air flow rate tends to quench the operation at the riser bottom. To overcome the above shortcomings of the single riser regenerator, multiple air inlet riser regenerator is introduced. In the present system air necessary is split and supplied them at different levels along a single riser regenerator. This allows the riser to be operated at relatively high gas velocities with enough oxygen supply for the regeneration reactions in most parts of the riser but not too much to cause quenching at the riser bottom. This can also significantly increase the solids inventory in the riser, benefiting the reactions.

5.1 PROBLEM STATEMENT

The regeneration on catalyst in multiple air inlet riser regenerator is considered. And it is assumed the kinetics should be based on simple two steps leading directly to CO_2 and H_2O as sole products. The operating conditions remains same as that of single inlet riser regenerator except there are two inlets at 0.9m and 1.90m of lengths 0.1m where the velocity of air is 0.5m/s.

$CH_{12\alpha} + (1 + 3\alpha)O_2 \rightarrow CO_2 + 6\alpha H_2O$; (α= hydrogen to carbon mass ratio in coke)

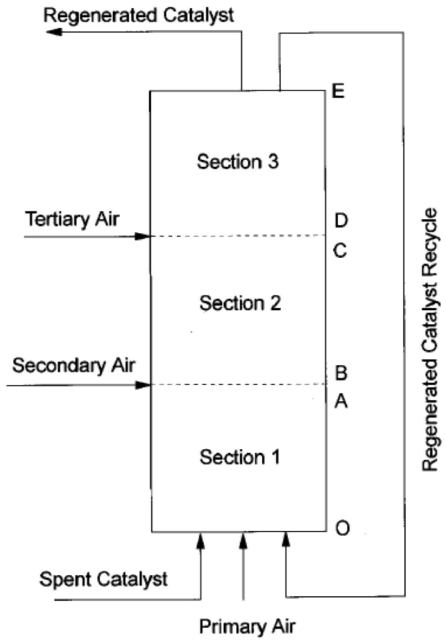

Figure 5.1: multiple air inlet riser regenerator (Bai et al., 1997)

5.2 FLUENT SIMULATION

5.2.1 GEOMETRY AND MESH

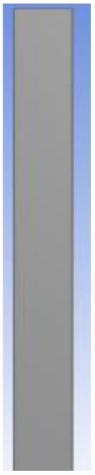

Figure 5.2: Geometry in Ansys workbench 13.0

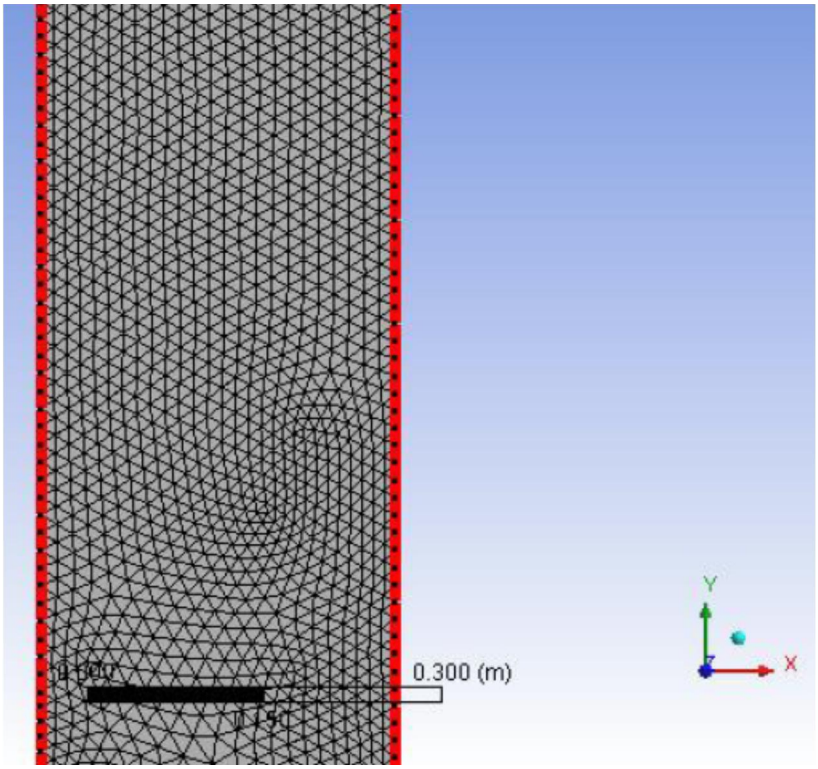

Figure 5.3: Meshing of geometry

5.2.2 BOUNDARY CONDITIONS

In order to obtain a well-posed system of equation, reasonable boundary conditions for the computational domain have to be implemented. At inlet velocity of the gas and coke is specified. Besides, the velocity at various inlets at the wall is also specified. Mass flow rate of catalyst and mass fraction of the species are specified. At outlet pressure boundary condition is specified. No slip boundary condition is specified at the wall.

5.2.3 SOLUTION TECHNIQUES

In fluent, solver is set as segregated which solves the equation individually. Transient state simulation has been formulated. Here pressure based solver is used. The species transport model is considered. Laminar finite rate model is used to predict the reaction rate. The discretization scheme for momentum, turbulent dissipation rate, turbulent kinetic energy and all has been taken as first order upwind. The following under relaxation factors have been used for different flow quantities: pressure:0.1, density:1, body forces:1,momentum: 0.1,volume fraction:0.1,granulartemperature:0.2,nergy:0.1 and species: 0.1.The convergence criterion for continuity, velocity and species is 0.001.

5.3 RESULTS AND DISCUSSION

In this section transient state results are discussed. The concentrations of the species inside the regenerator along axial direction at specified positions are plotted keeping all the conditions same as in single air inlet riser regenerator. Further the variation of temperature profile along axial directions at specified positions is compared between single and multiple

air inlet riser regenerator. The carbon concentration is compared for various types of regenerators both from calculation and those from literature.

5.3.1 CONCENTRATION OF CARBON AND OXYGEN IN MULTIPLE AIR INLET RISER REGENERATOR

In the multiple air inlet system, air inlets have been provided at 0.9m and 1.9m height with a slit of dimension 0.10m.The side air inlet velocity is 0.5 m/s. The presence of extra air inlet increases the concentration of oxygen without changing the main air velocity. This helps in greater combustion of the carbon content present in the spent catalyst. In the figure the concentration of oxygen shoots at two places which show the presence of side inlet temperature. Further it has also resulted in lower coke/carbon content in the exit/regenerated catalyst.

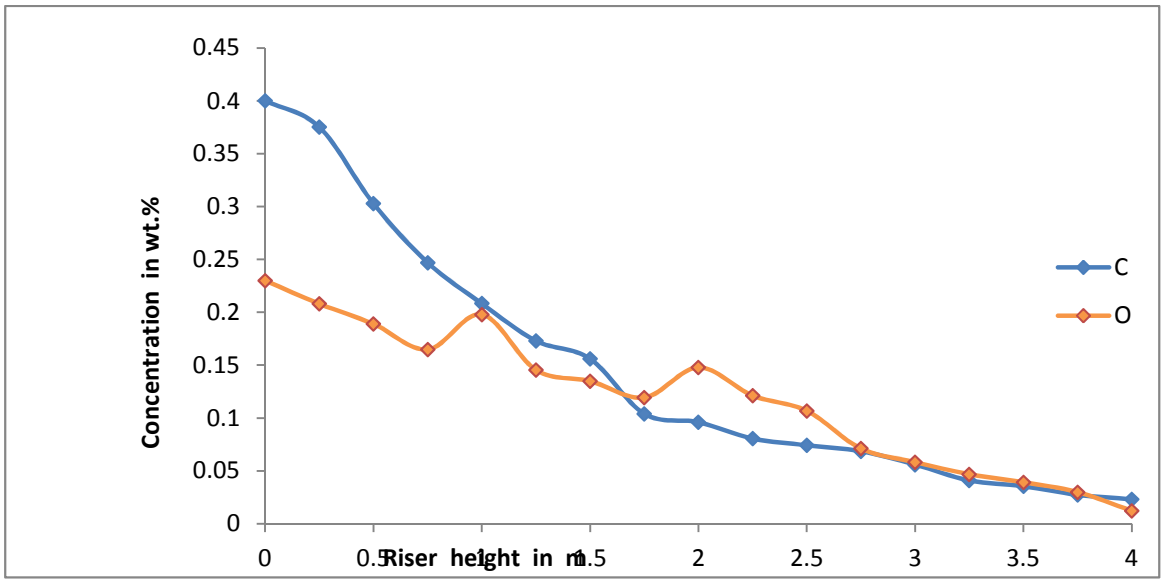

Figure 5.4: Concentration profiles of carbon and oxygen

5.3.2 VARIATION OF TEMPERATURE IN SINGLE AND MULTIPLE AIR INLET RISER REGENERATORS

The temperature inside the multiple air inlet riser is found to be less than single inlet riser. This is caused mainly due to the quenching of reaction products with cold air at the sides.

Thus keeping the system temperature at the controlled levels thereby preventing any thermal deactivation of catalysts due to invariable/sudden temperature rise. Further it also produces a less coke content regenerated catalyst. And removes any incomplete combusted gases.

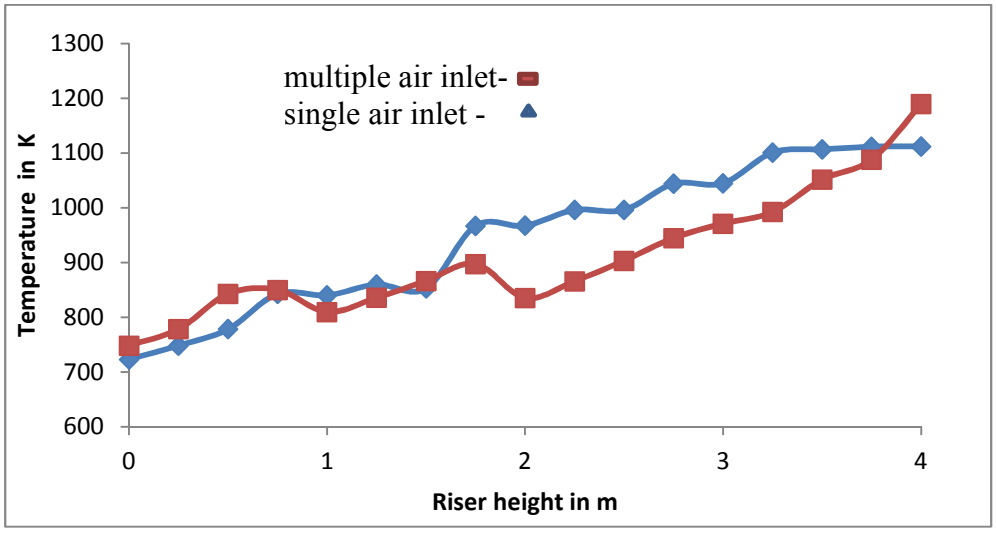

Figure 5.5 Comparison of temperature profile in single and multiple air inlet riser regenerators.

5.3.3 COMPARISON OF VARIOUS REGENERATORS IN TERMS OF CARBON COMBUSTION INTENSITY

The figure represents the comparison of the simulated riser regenerators from literature. The turbulent fluidised bed (Jian chang et al) and two stage riser regenerator (Bai et al) is compared with the simulated result. The single air inlet riser is found to give a better regeneration than turbulent fluidized bed for a given height and coke content. This is because there is better heat and mass transfer exchange right from the inlet while in fluidised bed there is dense phase at the bottom where the mixing is quite less than the single air inlet riser regenerator. However, the multiple air inlets is found to be having greater efficiency than single inlet due to the presence of oxygen rich air at various axial positions that enables proper mixing and greater combustion. The two stage riser regenerator developed by Bai et al is found to be the most efficient for high coke content catalyst as it is performed in two

separate stages where volatiles and hydrogen burns completely and in the second stage complete combustion of coke takes place.

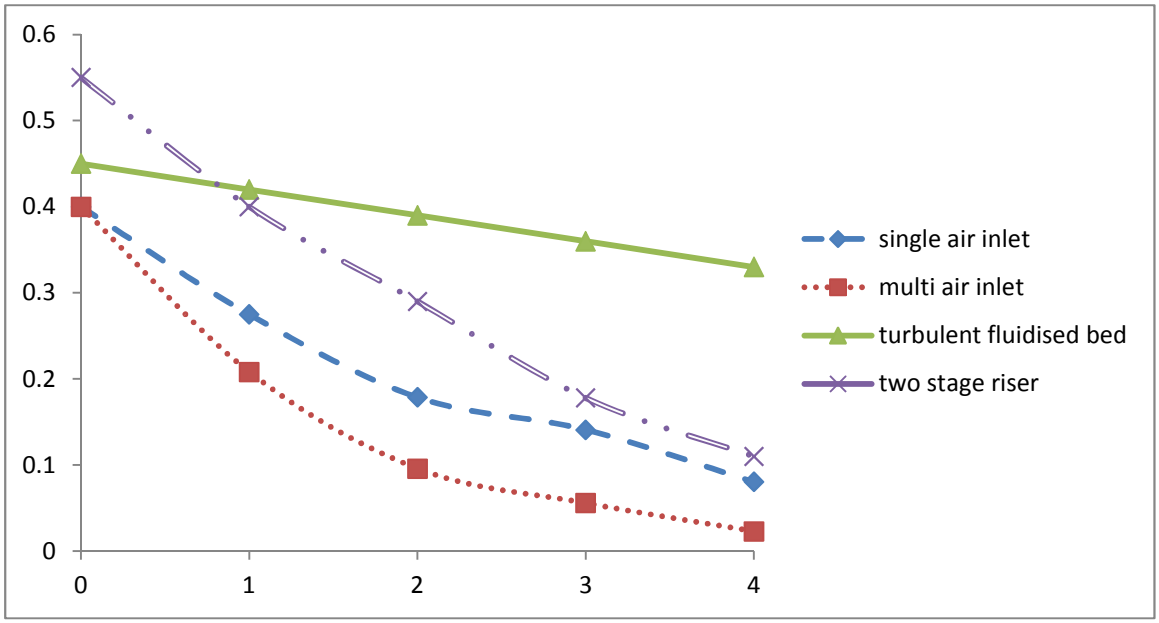

Figure 5.6 Comparison of coke combustion intensity in various regenerators (both simulated and theoretical)

5.4 CONCLUSION

A numerical study of riser regenerator is discussed. Regeneration of spent catalyst is taken as the model reaction. Key conclusion of this chapter can be summarized as follows:

- The carbon content in exit of the multiple air inlet regenerator is found to be less than that in single air inlet regenerator.
- Temperature profile along axial direction is found to have fluctuations due to the presence of multiple air inlets.
- Comparison of coke combustion capacity of various regenerator it's been found that it is function of riser height and for a given height two stage regenerator is found to have excellent coke combustion capacity followed by multiple air inlet riser regenerator.

CHAPTER 6

CONCLUSION

Chapter 6

CONCLUSION

In this chapter major conclusions of the present study work are summarized. The regeneration performance of novel riser regenerator is studied. The model incorporates the kinetic and hydrodynamic characteristics of FCC catalyst regeneration. Axial profile of temperature, oxygen concentration and coke content on the catalyst particles are predicted. Simulation indicated that FCC regeneration of catalyst is complex process influenced by many factors such as solid mixing, solids flow rate, velocity of air, coke content on spent catalyst. The performance of the single air inlet riser can be improved by splitting the air flow at several axial positions. The multiple air inlet riser regenerators are found to maintain regeneration and outlet temperature to that of industrial range. If the flow rate of air is maintained and provided at right axial positions better results will be obtained.

The following conclusions have been drawn from the riser regenerator:

- The species concentration decreases along the riser height.
- The temperature is affected by inlet velocity and it increases with increase in velocity till quenching temperature.
- Greater oxygen results in better regeneration.
- Solids void fraction is maximum at the bottom and decreases along the axial direction.

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